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ORIGINAL ARTICLE

TPO/TPD study on the activation of silica supported cobalt catalyst

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Abstract Silica supported cobalt catalysts have been prepared using urea containing cobalt nitrate solution impregnation method, which can give high loading Co_3O_4 with relatively smaller crystallite size. Compared to the conventional impregnation method, the catalyst prepared with urea added to the cobalt nitrate solution provides higher activity for CO conversion and C_5^+ selectivity. To optimize the catalyst activation and simulate the industrial activation, TPO–TPR cycle treatment with or without steam has been applied to the prepared catalysts under various conditions. It is shown that reduction of pure hydrogen with high flow rate leads to a sharp temperature rise in the catalyst bed, which results in the sintering of the cobalt particles. A slow temperature rise with dilute hydrogen helps stabilize the cobalt particles, and the cycle treatment of the catalyst using TPO–TPR without steam induction has little effect on the size of cobalt particles. When steam is included in the reduction stream with hydrogen the TPR–TPO cycle treatment can help increase the Co dispersion, which increases the catalyst activity and selectivity to C_5^+.

Keywords Supported cobalt catalyst · Fischer tropsch synthesis · Urea combustion · TPR-TPO

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Introduction

Research on alternative fuels plays an important role in emission reduction and future energy supply. Fischer–Tropsch synthesis possesses the ability to convert carbon containing sources such as coal, natural gas and biomass into a cleaner and more economical alternative to traditional commercial fossil fuel [1–3]. Many years-operational experiences have shown that the use of Fischer–Tropsch catalyst affects the economy of the whole process significantly. Therefore many researches have been undertaken to develop an efficient FTS catalyst, to refine the catalyst for the optimal activity [4–6]. Cobalt-based catalysts appear to provide the best compromise between performance and cost for the synthesis of hydrocarbon from syngas derived from coal, natural gas or biomass [7–13].

It has been demonstrated that metallic Co particles formed on the catalyst surface under FTS conditions are the origin of their catalytic activity for hydrocarbon formation [9, 13–17]. The supports for this process are primarily silica, alumina and titania, over which the active metal particles, e.g., cobalt, are dispersed. Co-based FTS catalysts are usually prepared by impregnating aqueous $Co(NO_3)_2{\cdot}6H_2O$ solution onto the support materials followed by drying and calcination. The impregnated Co nitrate is decomposed to Co_3O_4 and these precursor oxides are reduced with H_2 to Co^0 particles prior to FTS.

Recently, there have been studies showing that the activation procedure such as redox treatment can increase the catalyst performance.

On the other hand, there have been many efforts to make more uniform, stable and small Co_3O_4 particles over the support. These methods include the adaptation of calcination procedures and new Co precursors [14, 18, 19]. It is reported that Co oxalate and a mixed salt of Co nitrate and Co acetate as precursors give rise to smaller Co^0 particles over the support [20]. However, the use of these precursors produced significant amounts of Co silicate-like species simultaneously, which were hardly reduced to the metallic state under normal conditions. Therefore, reducibility of Co was suppressed greatly, resulting in only weak activity enhancements.

To give a higher Co loading with better dispersion, chelating agents with multi-impregnation steps have been studied, which can give high Co loading with relatively small Co particles. However, this process is time consuming and difficult to scale up. Recently we have developed a novel method, which is to use the minimum amount of water and urea to form a Co nitrate containing aqueous organic solution. The feature of this solution is that it has high stability and high Co content, which easily leads to high Co content in the resulting catalysts [18, 21–26].

In this work, we prepared silica supported cobalt catalysts using the urea–cobalt nitrate hydrate system and silica support, and also the conventional aqueous impregnation method for comparison. The catalysts have been tested and characterized using various techniques, and their performances have been compared. The catalyst activation method on the chemical and physical properties of the urea-assisted dispersed catalyst has been explored [20, 27, 28].

Experimental setup

Catalyst preparation

The catalyst has been prepared according to the process described in the patent [29]. High surface silica (Fumed silica, Industrial Grade, Aldrich) is used as the support. Due to the nature of the fumed silica, it is wetted with very dilute $Al(NO_3)_3$ (analytical grade, Aldrich)/HNO_3 solution (0.001 M) to form a paste and dried at 350 °C. This support was used in all the experiments. The active metal comes from Co nitrate. The urea–cobalt melt solution is prepared as follows:

$Co(NO_3)_2{\cdot}6H_2O$ (Alfa, analytical grade) was mixed with $ZrO(NO_3)_2{\cdot}2H_2O$ (Alfa, Chemical Grade) (Co:Zr = 10:1, atomic ratio), and urea was added in a 4:1 ratio of urea to cobalt metal; the resulting mixture was then heated to 60 °C and stirred. The main action of zirconia is to reduce the cobalt reduction temperature as shown in the literatures [30–32]. A minimum amount of water (2.0 ml) was added to the mixture to make a solution. The cobalt nitrate and zirconium nitrate were dissolved completely after stirring for 3 h at 60 °C, the mixture was assumed to be homogeneous, and then the dried fumed silica (surface area 605 m^2/g; particle size 250–350 μm) was added to the solution for 24 h. The mixture was stirred to allow the support to contact the solution. The mixture was heated at approximately 50 °C to vaporize the excess water in the mixture. It was then transferred to a quartz boat and calcined at 350 °C in static air for 10 min. The resulting black particles were the catalyst precursors with a cobalt loading of 28.0 wt% over the silica support. The material prepared in this way is denoted as $Co/SiO_2–ZrO_2–urea$.

For comparison, the non-urea added silica supported Co catalyst was prepared by incipient wetness impregnation of aqueous cobalt nitrate and zirconium oxy-nitrate in the fumed silica support, the system is placed in static air for 6 h at ambient temperature, and then dried at 200 °C for 4 h and calcined at 350 °C for 4 h to get a supported cobalt catalyst [33, 34]. To increase the cobalt content, the calcined sample is re-impregnated with the Co and Zr nitrate solution. The same treatment process was repeated to prepare the catalyst with Co_3O_4 loading up to 28.0 wt%. The catalyst prepared using this method is denoted as $Co/SiO_2–ZrO_2–IC$.

Catalyst tests

In the catalyst evaluation, 0.4 g (in powder form) was loaded in a 9 mm (OD 6 mm id) quartz tube. A stream of H_2 (99.9 % from Air Products) flow was passed through the catalyst at a GHSV of 5,000–8,000 h^{-1} under atmospheric pressure before reaction. The temperature ramp rate was 1 °C/min to 400 °C and held for 2–4 h, then cooled to 225 °C, at which the syngas ($H_2/CO = 2$, with 5 vol% N_2 as the internal standard, supplied by Air Products) was conducted into the reactor. The activity test was started under high pressure ($\sim$8 bar). The duration of the reaction depends on the catalyst performance, but would not be longer than 20 days. The exit gas was sampled every 30 min and analyzed using an on-line GC (Aglient 5890).

Catalyst characterization

TEM measurements were carried out on a JEOL 2010 analytical electron microscope, which had a LaB_6 electron gun and could be operated between 80 and 200 kV. This instrument had a resolution of 0.19 nm, an electron probe size down to 0.5 nm and a maximum specimen tilt of ±10° along both axes. The instrument was equipped with an

Oxford Instruments LZ5 windowless energy dispersive X-ray spectrometer (EDS) controlled by INCA. It had facilities for point analysis as well as mapping and line scanning through the SemiStem controller.

Catalyst activation was optimized using TPR–TPO redox treatment. To simulate the activation process, the first TPR experiments used 100 $\%H_2$ (wet or dry) as reducing gas, at 15 ml/min to give a GHSV $\sim$9,000 h^{-1}. After the first TPR treatment, the catalyst was then oxidized with approximately O_2 5 vol% in helium using temperature programmed oxidation. After the first round TPR–TPO, the other TPR experiments adopted 5.02 $\%H_2$/He 50 ml/min at 1 °C/min temperature ramp rate to the final reduction temperature and time.

The TPO experiments were carried out using 5.02 $\%O_2$/He as oxidizing gas, the temperature ramping rate was set at 5 °C/min temperature ramp rate, 400 °C for 2 h. During the cobalt oxide catalyst reduction, there was steam vapor generated, which may affect the cobalt particle and catalyst structure. So in this work, water vapor was co-fed with the hydrogen stream. The experimental details with water vapor are as follows:

The chemisorption machine was modified for co-feeding water vapor with hydrogen stream. H_2 passes through the water saturator under controlled temperature to generate water vapor-saturated H_2 stream for catalyst reduction during first TPR. The water saturator was set at 30 °C to generate 4.2 $\%H_2O/H_2$ stream.

The crystalline structure of the catalyst was analyzed using X-ray diffraction (Philips X-PeRT Pro Alpha I) operating with $Cu_K\alpha$ radiation ($\lambda = 1.5406$ Å) at a tube current of 40 mA and a voltage of 45 kV with speed of 0.02/S.

Results and discussion

Catalyst test

The catalysts prepared with and without urea in the aqueous solution were tested for Fischer–Tropsch synthesis, and the results are shown in Figs. 1 and 2. It is noted that the relatively sharp change of the activity and selectivity is the consequence of the empty liquid trap which caused pressure change, but this does not change the general trend of the catalyst performance.

For the Co/SiO_2–ZrO_2–IC catalysts, the CO conversion is about 67 % at the start of reaction at 220 °C, 8 bar with GHSV of 1,500 h^{-1}, but the CO conversion decreases rapidly in the first 8 h and then gradually drops to 58 % in 50 h time on stream, suggesting that the catalyst activity decreases; it is not stable, although the C_5^+ selectivity is about 75 % and almost remains unchanged during the test.

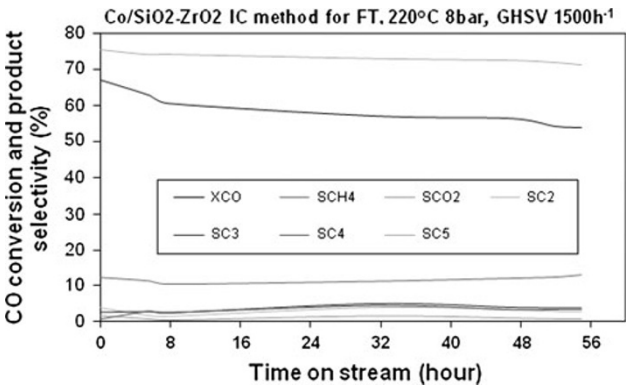

Fig. 1 FT test results of the Co/SiO_2–ZrO_2–IC

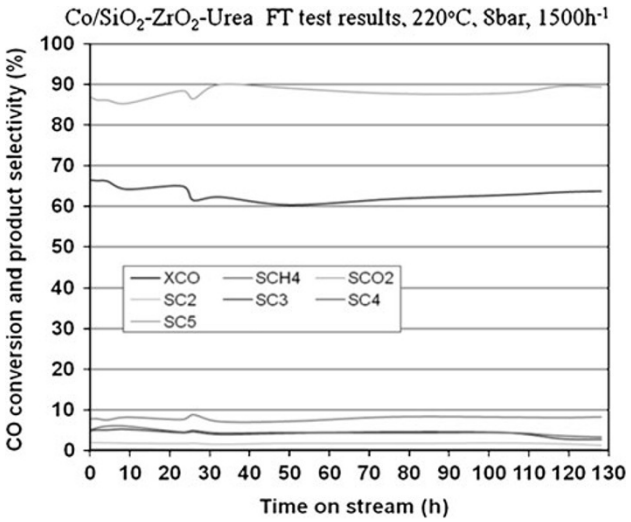

Fig. 2 FT test results of the Co/SiO_2–ZrO_2–urea

The methane selectivity is more than 10 % and slightly increase after the catalyst is tested for 50 h.

Over the Co/SiO_2–ZrO_2–urea catalyst under the same conditions, CO conversion is 67 % at the start of time on stream, and gradually decreases to 61 % in the first 10 h, and then becomes stable afterward. Compared to the catalyst prepared without urea, the catalyst prepared with urea has the following advantages: the CO conversion keeps above 62 % in the 180 h of time on stream, and the selectivity to C_5^+ is about 90 %, and remains almost unchanged, the methane selectivity is less than 10 %.

Comparison of Figs. 1 and 2 suggests that the silica supported catalyst prepared with urea clearly has higher stability, and better selectivity to C_5^+. The addition of urea in the cobalt nitrate impregnation stage improves the Co particles' dispersion over the silica support.

The differently prepared catalysts' properties are shown in Table 1. It is shown that the loading of the cobalt oxide over the silica support decreased the catalyst surface area from 652 m^2/g to about 350 m^2/g, and the pore size and

Table 1 The physical properties of the different prepared Co catalysts

Support	Calcination T °C	BET SA (m^2/g)	PV (cm^3/g)	Pore size (nm)	Co_3O_4 particle size	Reduced Co particle size (nm)
SiO_2 support	350	652	1.65	16		
Co_3O_4/SiO_2–ZrO_2 IC	350	345	1.31	14.0	19.5	15
Co_3O_4/SiO_2–ZrO_2 urea	350	375	1.32	13.4	13.3	10.2

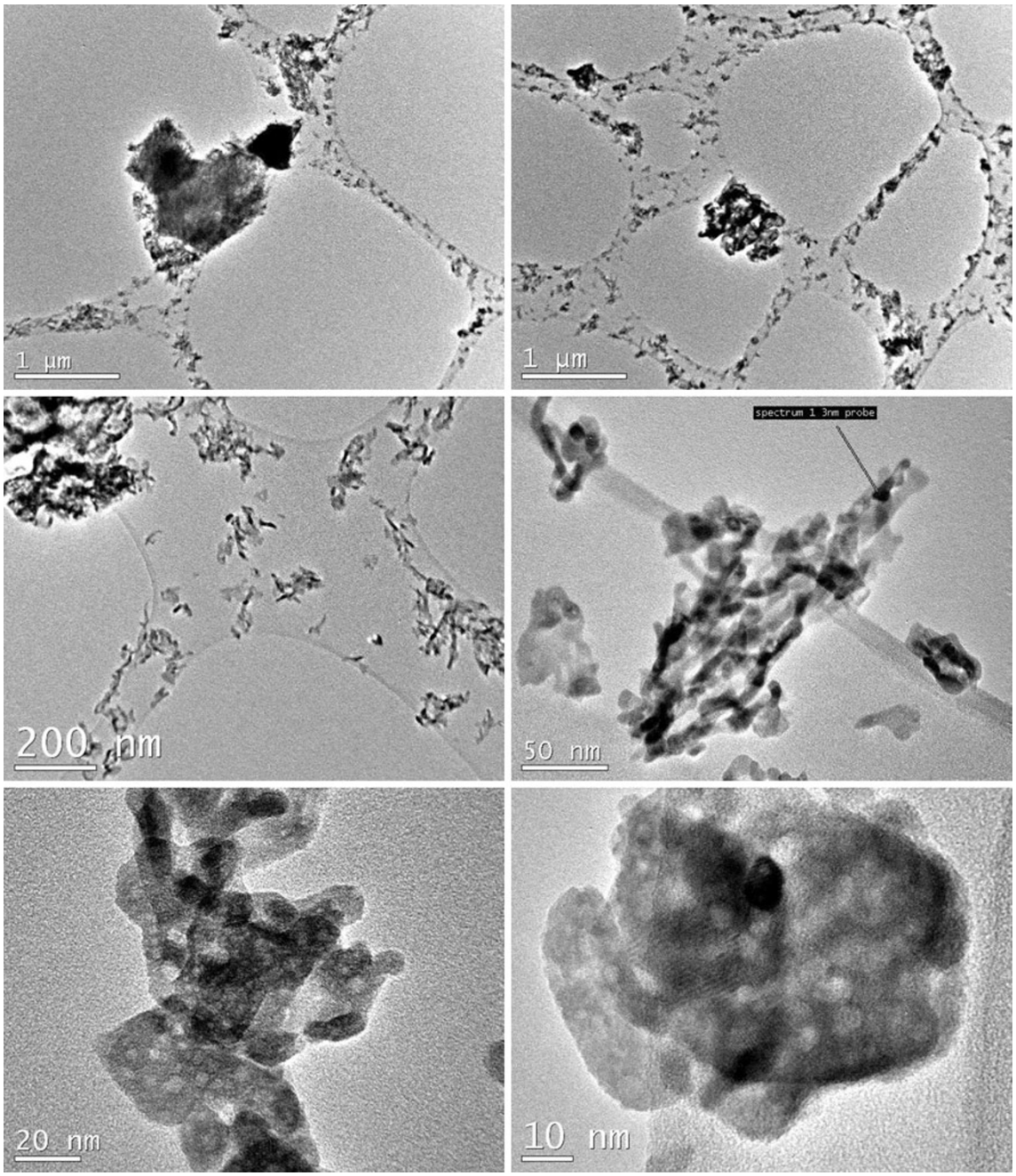

Fig. 3 The TEM image of Co/SiO_2–ZrO_2 catalysts prepared without urea

pore volume all drop accordingly; this may be due to the fact that cobalt particle occupies the pores and wall of the pore of the support. The cobalt particles before and after reduction were measured using TEM and XRD; it is shown that the main phase of cobalt over the catalyst before activation in the Co/SiO_2–ZrO_2–IC is 19.5 nm, and that

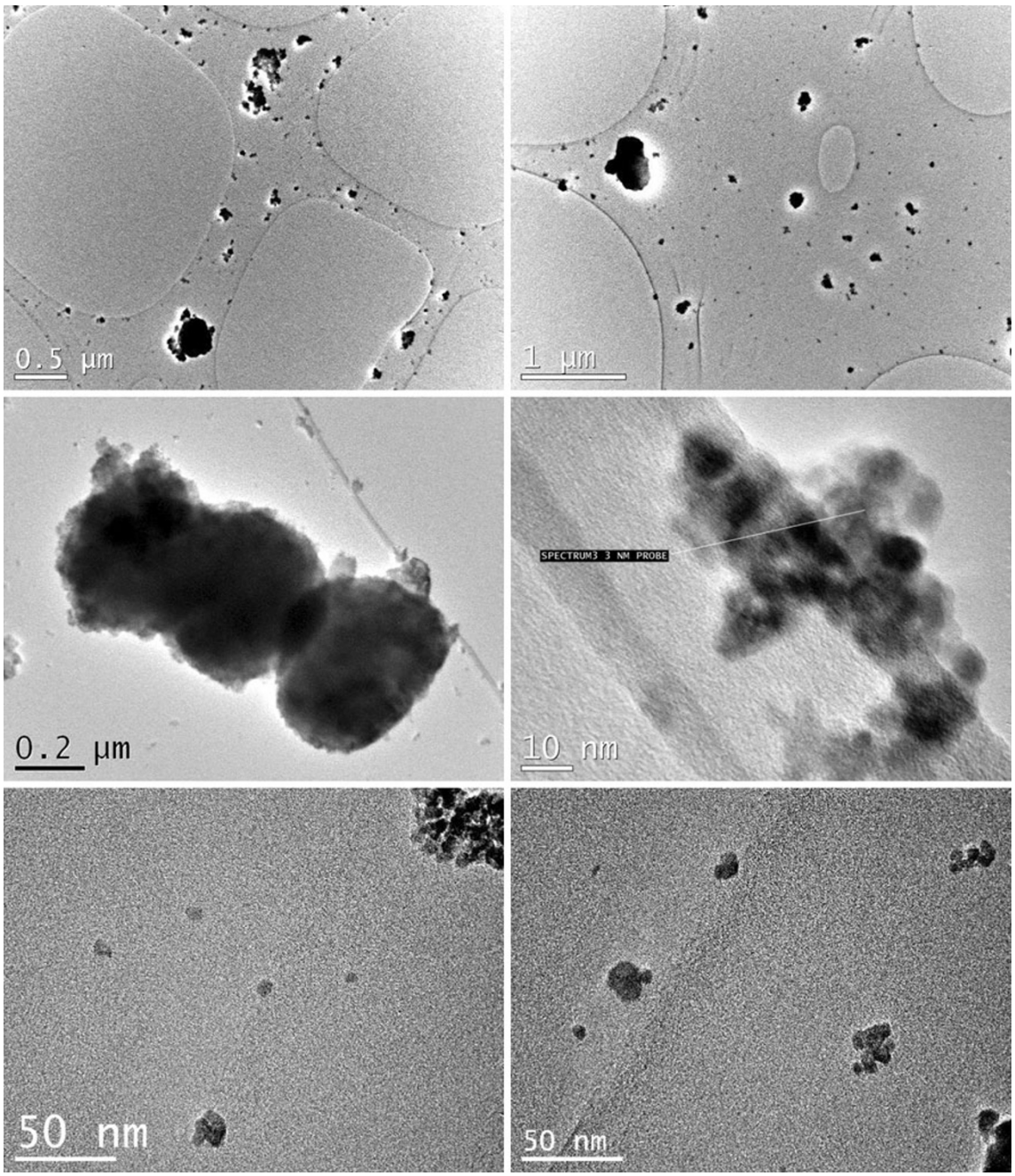

Fig. 4 TEM images of the $Co/SiO_2–ZrO_2$–urea catalyst prepared using urea melted method after calcinations at 350 °C

Table 2 TPO and BET data of the TPO–TPR treated catalysts

Run	TPO peak temperature (°C)	O_2 uptake (cm^3 STP/g)	BET surface area (m^2/g)
TPO_1	182.5	63.06	–
TPO_2	165.7	57.87	–
TPO_3	161.9	57.10	–
TPO_4	160.1	55.78	284.6 ± 1.2

over the urea containing catalyst $Co/SiO_2–ZrO_2$–urea is 13.3 nm. After the hydrogen reduction of the catalyst, cobalt is converted into cobalt metal, which changes to 15 nm over the $Co/SiO_2–ZrO_2$–IC and 10.2 nm over $Co/SiO_2–ZrO_2$–urea. This suggests that the addition of urea during the catalyst preparation can help have a higher dispersion of the cobalt oxide and cobalt metal over the silica supported catalyst.

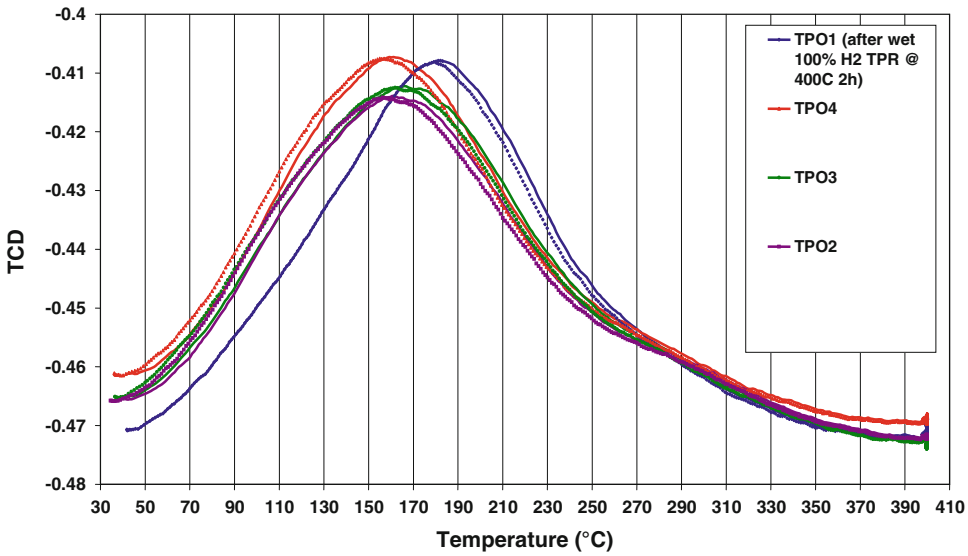

Fig. 5 TPO results of the Co/SiO_2–ZrO_2–urea during the TPR–TPO cycle treatment; *double lines* indicate the reproducibility of the TPR–TPO setup

Table 3 TPR data of Co/SiO_2–ZrO_2–urea

Run	TPR peak temperature (°C)	Total H_2 uptake (cm^3 STP/g)[a]
TPR_2	129.6/246.0	167.57
TPR_3	133.3/235.2	168.92
TPR_4	134.8/235.9	170.28

[a] TPR integration is not as accurate as TPO due to the fact of cold-trap warm up with time and the disturbance of profile, while changing cold trap during the run

Characterization of the catalysts prepared with and without urea using TEM

To study the effect of urea on the catalyst preparation and explore the catalytic differences between Co/SiO_2–ZrO_2–IC and Co/SiO_2–ZrO_2–urea, the catalyst after calcinations has been characterized using TEM, and the results are shown in Figs. 3 and 4.

For the silica supported cobalt catalyst without adding urea, after drying before the calcination, XRD measurement showed that the cobalt is partly dehydrated to cobalt nitrate, the cobalt nitrate hydrate re-crystallizes when the water is vaporized even when it is dispersed in the high surface area support.

For the catalyst supported with urea added in the Co nitrate solution, where much excessive urea is added to form a melt urea–$Co(NO_3)_2$ solution, it is impregnated with the silica support and the mixture is dried at 50 °C for 6 h, and the XRD results of the dried sample show no diffraction peaks, suggesting that the cobalt nitrate did not re-crystallize when co-impregnated with urea.

The TEM observation results revealed that most particles in the Co/SiO_2–ZrO_2–IC were small aggregates (10–100 nm) of elongated primary particles. Some micrometer-sized aggregates could also be seen. Many of

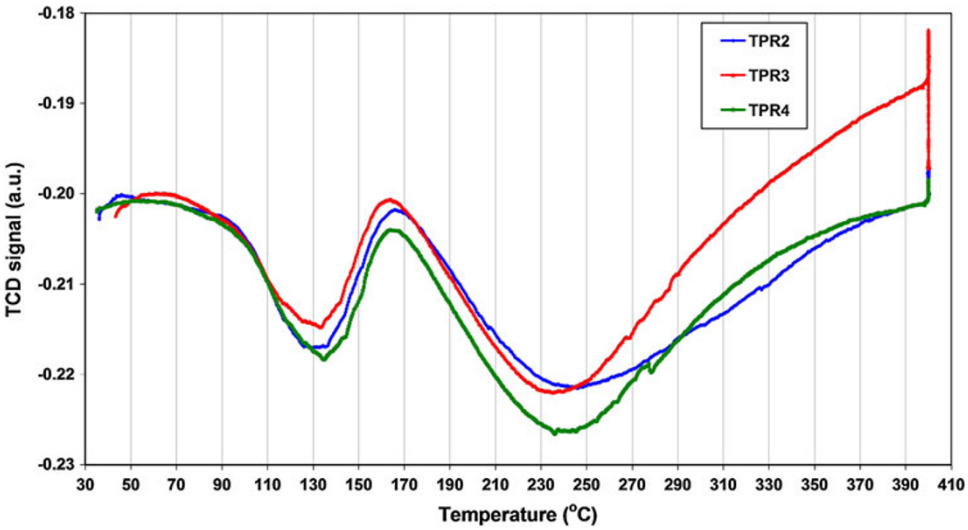

Fig. 6 TPR profiles of the Co/SiO_2–ZrO_2–urea catalyst during the TPR–TPO cycles treatment with the wet hydrogen

Table 4 TPO and BET data

Run	TPO peak temperature (°C)	O_2 uptake (cm^3 STP/g)	BET surface area (m^2/g)
TPO_1	172.5	65.55	–
TPO_2	163.8	59.65	–
TPO_3	166.7	61.02	282.0 ± 1.2

the cobalt oxide particles are needle like, which are very close to the cobalt nitrate precursor crystallites. It is also found that small aggregates and single particles are in crystalline form, the broad particle size distribution may be the reason for the relatively low selectivity [7, 14, 35]. EDX studies with a 3-nm probe gave a Co to O ratio of approx. 55–45 %.

The $Co/SiO_2–ZrO_2$–urea sample has different TEM observation from the $Co/SiO_2–ZrO_2$–IC. Most particles over the urea melted catalysts have small aggregates (diameter 5–50 nm), but some micrometer-sized aggregates could also be seen. Compared to the Co nitrate sample without urea, these aggregates appear more isometrical and generally more single particles could be seen. Small aggregates and single particles are in crystalline form, but smaller than the conventional impregnated method, and with some potential porosity in the particle. The EDX studies of 3 nm probes gave a Co to O atomic ratio of 58–42 %, suggesting that some cobalt might be reduced by the urea during the calcinations.

Figures 1 and 2 showed that the urea melting method gave higher FT catalyst stability and C_5^+ selectivity. Given that much more excessive urea is added in the catalyst preparation, there maybe some amount of carbon residue in the catalyst, which may be removed by TPO–TPR treatment, it has also been shown that the TPO–TPR cycle treatment of the cobalt catalyst can increase the catalyst dispersion [36–38]. And for the cobalt catalyst prepared using urea melt cobalt salt method, the optimization of the catalyst activation may be able to improve the catalyst performance. To reach a better catalyst performance, therefore in the following work, we will employ TPR–TPO treatment of the $Co/SiO_2–ZrO_2$–urea and to characterize the catalyst Co dispersion and H_2 pickup so as to explore the optimized conditions for the catalyst activation.

TPO/TPR cycle study for catalyst activation optimization

Wet H_2 TPR_1 (400 °C 2 h) followed by TPO_1/TPR_2/TPO_2/TPR_3/TPO_3/TPR_4/TPO_4

This experiment was performed by wet H_2 reduction (TPR_1: H_2 GHSV = 8,740 h^{-1}, 4.2 vol% H_2O) followed by normal TPO/TPR as described above. The TPO results are presented in Table 2 and Fig. 5. The TPR results are presented in Table 3 and Fig. 6.

It is seen that the TPO_1 after wet H_2 reduction shows higher TPO peak temperature and more O_2 uptake than the sequential TPOs. TPO_2, TPO_3 and TPO_4 have similar peak temperature and O_2 uptake, but all of them are lower than TPO_1. The oxidation peak temperatures of TPO_2, TPO_3 and TPO_4 are also lower than TPO_1. These results suggest that the first pure H_2/H_2O reduction reduce more cobalt oxide into cobalt metal with bigger particle size, and the followed oxidation, then 5 %H_2/Ar reduction may further reduce the particle size, which becomes easier to be oxidized. But the reduction gas stream, e.g., 5 vol% H_2 may not be able to reduce the cobalt oxide into metal, hence it has less O_2 pickup in the followed TPO cycles.

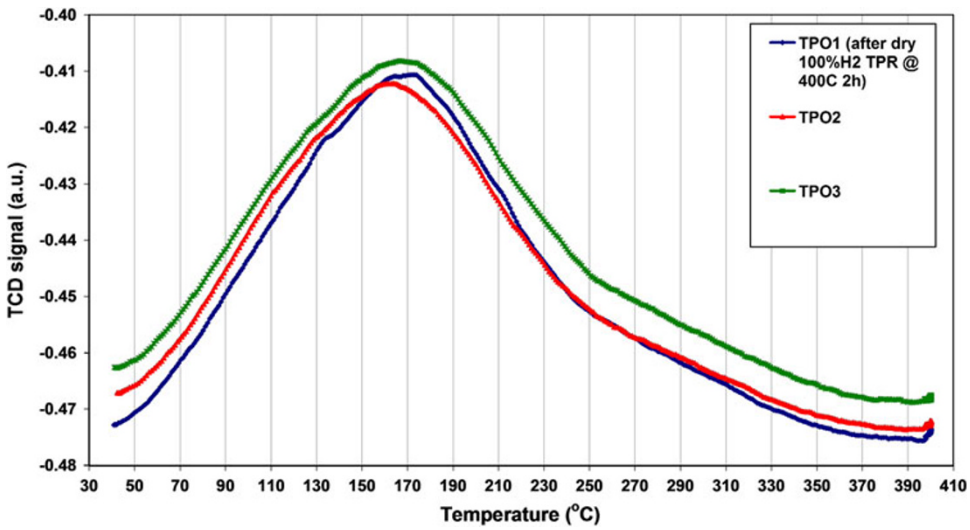

Fig. 7 TPOs profiles of the $Co/SiO_2–ZrO_2$–urea catalyst firstly reduced with dry hydrogen (no water vapor is brought in with H_2)

Table 5 TPR data

Run	TPR peak temperature (°C)	Total H_2 uptake (cm^3 STP/g)
TPR_2	130.1/239.2	169.8
TPR_3	139.2/242.4	200.8

After wet H_2 reduction cobalt is more difficult to re-oxidize than that reduced under dry 5 %H_2/Ar. And there is more Co reduced in wet H_2 reduction than consequential TPRs. This may be explained by the fact that the in the first wet-reduction, hydrogen is almost in pure stream, which can reduce more cobalt than the TPR_2 that used 5 vol% of H_2 in argon, the cobalt reduction may not be achieved completely with 5 vol% H_2/Ar.

The surface area of the Co/SiO_2–ZrO_2–urea changed to about 284.6 m^2/g after the TPR–TPO cycle treatment, which might result from the cobalt oxide reduction.

It is to be noted that TPR_1 is not shown here, because it is carried out in pure hydrogen stream at temperature programmed way; however, the TCD detector cannot respond to the change of pure hydrogen stream, no report of TPR_1 is given.

In the TPR profiles of the Co/SiO_2–ZrO_2–urea during the TPR–TPO cycle treatment, we can see that TPR_2 shows lower peak temperatures and less H_2 uptake than TPR_3 and TPR_4. TPR_3 and TPR_4 show similar peak temperatures. However, after TPR/TPO treatment cycles, the first cobalt reduction peak temperature shifts slightly higher, while the second cobalt reduction peak temperature shifts lower. This suggests that the overall cobalt interaction with support may be weak; however, some cobalt particles may become smaller, hence the first reduction peaks shift upwards.

It is interesting to see that after the redox treatment, H_2 uptake amount is significantly higher, suggesting that cobalt dispersion increases after the treatment.

Dry H_2 TPR_1 (400 °C 2 h) followed by TPO_1/TPR_2/TPO_2/TPR_3/TPO_3

This experiment was performed by dry 100 %H_2 reduction (TPR_1: H_2 GHSV = 8,680 h^{-1}) followed by normal TPO/TPR as described above. The TPO results are presented in Table 4 and Fig. 7. The TPR results are presented in Table 5 and Fig. 8.

We can see that the TPO_1 after dry 100 %H_2 reduction shows higher peak temperature and more O_2 uptake than the sequential TPOs. TPO_2 shows lower peak temperature and less O_2 uptake than TPO_3. This result is very similar to that of wet H_2 reduction; however, TPO_1 peak temperature is about 10 °C lower than wet H_2 reduction case. And the higher O_2 uptake in TPO_1 of the dried H_2 reduced sample (65.55 cm^3 STP/g) is due to the better reducibility of the dry-hydrogen stream.

Although the peak temperature of TPO_3 shifts a little higher, it is still lower than TPO_1, suggesting that the redox treatment makes it easier for cobalt metal to be oxidized.

It is seen that TPR_2 shows lower peak temperatures and less total H_2 uptake than TPR_3. This is not consistent with the one pre-reduced with wet-hydrogen stream. In the wet-hydrogen treatment catalyst, the first cobalt reduction peaks shifts to higher temperature, which is similar to the dry-hydrogen system; however, the second cobalt reduction peak maxima temperature shifts to lower end, which easily reduces the catalyst completely. The higher H_2 uptake of TPR_3 suggests that the redox treatment significantly increases the cobalt dispersion.

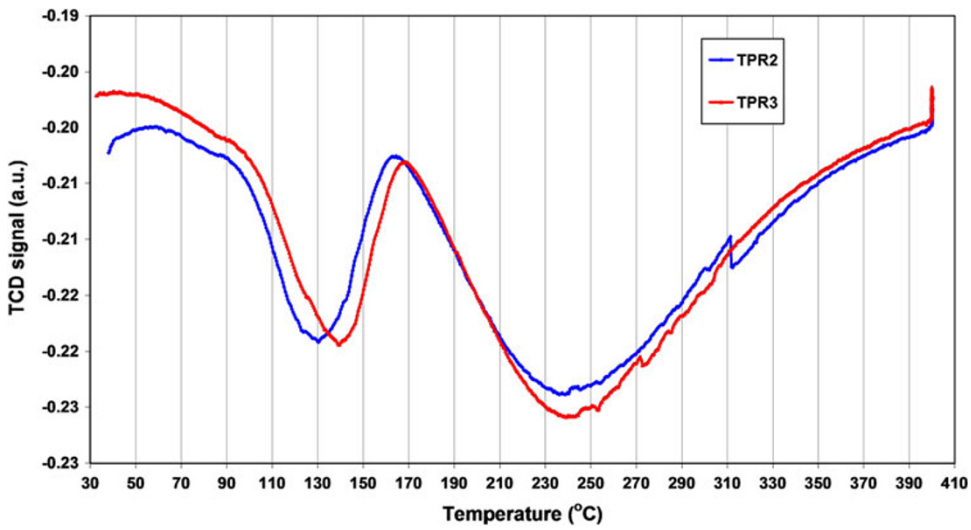

Fig. 8 TPRs profiles of the Co/SiO_2–ZrO_2–urea firstly reduced with dry H_2 and then TPO–TPR cycle treatment

Table 6 Comparison of the effect of redox treatment on the FT performance of the Co/SiO_2–ZrO_2–urea catalyst

Catalyst treatment	Dry H_2 reduction to 400 °C	Redox with wet H_2 (water vapor)	Reduced with dry hydrogen, then three cycles redox treatment
CO conversion (%)	63.6	65.2	64.1
C_5^+ selectivity (%)	88.6	89.1	88.9
CH_4 selectivity	8.3	8.4	8.3

Catalyst test conditions: 220 °C, 8 bar, GHSV 1,200 h^{-1}, H_2/CO = 2:1, the data were obtained after 20 h time on stream

Also the cobalt dispersion in the dry-hydrogen treated system is higher than that in the wet-hydrogen pre-treated system.

Table 6 shows the catalyst test results of the Co/SiO_2–ZrO_2–urea using different activation methods, it is also shows that the redox treatment leads to different H_2 pickup and the reduction temperatures, the CO conversion only slightly increases with the water vapor-containing H_2 and then redox treatment, changing from 63.1 to 65.2 % of CO conversion, while the dry H_2 treatment catalyst increases less Co conversion than the water vapor-containing H_2 stream. In terms of C_5^+ selectivity, there are little differences; all the catalysts with different activation have C_5^+ selectivity of 90 %. These results suggest that the activation with redox treatment may have a little improvement on the catalyst activity, but with almost no effects on the product selectivity.

Conclusion

1. Silica supported Co catalysts promoted with ZrO_2 have been prepared with and without urea addition to the cobalt solution. It is shown that the catalyst prepared with urea added to the cobalt precursor has higher activity for Co conversion and C_5^+ selectivity under the test conditions. Also the catalyst is more stable.
2. TEM results showed that the addition of urea in the cobalt solution makes cobalt oxide particle smaller and more uniform. The main phase of cobalt after the calcinations is Co_3O_4.
3. In the catalyst activation of Co/SiO_2–ZrO_2–urea, the initial reduction conditions using 100 % H_2 have a significant effect on following TPO_1. The effect on TPO_1 peak temperature follows the order: "wet 100 %H_2 400 °C 2 h (182.5 °C)" >dry 100 %H_2 400 °C 2 h (172.5 °C).
4. The pre-reduction atmosphere has effect on the cobalt reduction after TPO treatment. When water vapor is present in the hydrogen stream, the first H_2 TPR peak shifts to higher temperature, but the second H_2 TPR peaks shifts to lower temperature after redox treatment. When dry hydrogen is used for pre-reduction, both TPR H_2 reduction peaks shift to higher temperature.
5. Redox cycle treatment leads to higher cobalt dispersion, which is reflected by the increase of H_2 uptake in the TPR_2 files. The dry H_2 reduced at 400 °C gives the highest cobalt dispersion after two cycles of redox treatment, while pre-treatment with wet hydrogen gives the lowest H_2 uptake after the two cycles of redox treatment.
6. Although redox treatment helps increase the reducibility of the cobalt in the catalyst, the catalyst performance improvement is not so significant, there is slightly better CO conversion, while the C_5^+ selectivity remains almost unchanged among the catalyst.

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